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COMMUNICATIONS

Antibunching in the Emission of a Single Tetrachromophoric Dendritic System

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Investigations of the fundamental aspects of energy-transfer processes are relevant for multichromophoric systems such as photosynthetic complexes and conjugated polymers.[1] These systems are becoming increasingly accessible by single-molecule spectroscopy (SMS)[2−5] which can provide detailed information on the spatial, conformational, and temporal inhomogeneity of populations that are otherwise lost due to averaging. One intriguing phenomenon that is resolved by SMS is collective intermittences in the fluorescence of multichromophoric systems such as conjugated polymers and multichromophoric dendrimers.[3−5] Collective off-states are ascribed to the formation of nonfluorescent traps,[3] either due to reversible reactions with oxygen[4] or singlet−triplet annihilation.[5] Dendrimers decorated with chromophores at the periphery are systems that possess a large absorption cross-section and show energy hopping of the exciton among the chromophores. They are easily tunable in size, geometry, and chromophore number, thus enabling the investigation of many photophysical phenomena. The multichromophoric system targeted in this communication is a shape-persistent polypheneylene dendrimer (**1**) with a tetrahedral core and four peryleneimide (PI) units at the rim (Figure 1).

Perylenimide is a well-known chromophore that is well suited for SMS due to its high photostability, extinction coefficient ($\epsilon = 38300$ L mol^{-1} cm^{-1} at $\lambda_{max} = 495$ nm), and fluorescence quantum yield ($\Phi_f \approx 1$). The tetrahedral core and polypheneylene arms ensures a rigid structure with the chromophores distributed at the rim such that interchromophore electronic interactions are limited to weak coupling (distance $\approx$ 3 nm).

With four closely spaced chromophores, it is expected that each of the chromophores can absorb light, but due to excited-state energy hopping, it is not necessarily true that each of the four emits light. In this communication, we report on the probability that multiple photons are emitted from **1** after multiple photons are adsorbed by the system. We confirm that multiple chromophores on a single dendrimer absorb light using rotating linearly polarized excitation light and analyzing the total emitted fluorescence in time. A single PI chromophore has a well-defined absorption dipole, and the emitted fluorescence drops to the background when the linear polarization of the excitation beam is oriented perpendicular to the absorption dipole. For multiple chromophores with nonparallel absorption dipoles, the fluorescence will not drop to the background regardless of the polarization angle of excitation.

The number of independent emitters present in the detection volume can be determined by measuring the distribution of interphoton times in a manner similar to classical anti-bunching experiments. For a single emitter, the probability of emitting two consecutive photons drops to zero for time intervals shorter than the excited-state lifetime. In simple terms, the molecule cannot emit two photons simultaneously. After photon emission, a molecule must be re-excited and wait, on average, one fluorescence lifetime before another photon can be emitted. For sufficiently short laser pulses the number of photon-pairs detected per laser pulse can be used to determine whether the emission is from one or more independently emitting quantum systems. A recently developed method for the analysis of interphoton times using the classical Hanbury-Twiss and Brown coincidence setup in combination with pulsed excitation[6,7] (488 nm, 8.18 MHz, 1.2 ps fwhm, 2.1kW/cm^2) was applied to determine the number of emitting chromophores on single PI dendrimers. To record single-molecule fluorescence transients, single dendrimers were selected from an image scan and positioned in the laser focus of a confocal microscope. After collection of the fluorescence by the same objective, the signal is separated by a 50/50 beam splitter and focused onto two detectors (APDs). Samples were prepared by spin-casting a solution with an appropriate concentration of dendrimers dissolved in toluene containing 1% poly(methyl methacrylate) onto glass cover slides. All measurements were carried out at ambient conditions. In a first run, using a rotating $\lambda/2$ waveplate, rotating linearly polarized laser light was used for excitation (Figure 2). For a single chromophore (or several chromophores with parallel transition dipoles), the detected fluorescence would obey a cos^2 law as indicated by the gray plot. The demodulation of the fluorescence intensity indicates that more than one absorber with nonparallel absorption dipoles are present.

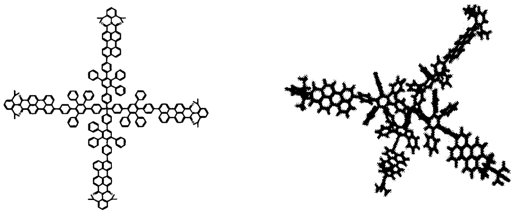

Figure 1. Two- and three-dimensional structures of the polyphenylene dendrimer decorated with four perylenimide chromophores.

After several modulation cycles, the excitation beam was blocked, and a $\lambda/4$ waveplate was inserted in place of the $\lambda/2$ waveplate to generate circularly polarized excitation light. The fluorescence intensity and the interphoton distances were measured for the same dendrimer molecule (Figure 3A). Several intensity levels in the transient indicate successive photobleaching of individual PIs. As observed in previous studies of multichromophoric systems,[3] after

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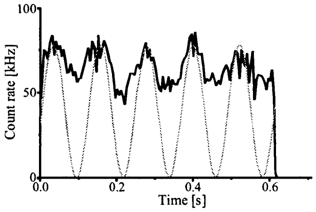

Figure 2. Fluorescence transient for a single molecule of **1** using modulated linear polarized excitation (black). The gray curve shows the modulation in fluorescence intensity expected for a single chromophore.

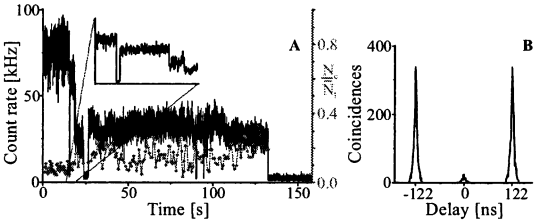

Figure 3. (A) Fluorescence intensity transient (black) and $N_\mathrm{c}/\overline{N}_\mathrm{l}$ ratio transient (gray) of the same dendrimer as in Figure 2 using circular polarized excitation (2.1 kW/cm^2). (B) Interphoton distance (coincidence) histogram for the first intensity level (15 s) of the transient in (A).

~15 s, a collective off-state occurs (inset of Figure 3A). Figure 3B shows the distribution of interphoton times collected during the first intensity level. The central peak of the distribution at a delay time of 0 ns corresponds to photon pairs induced by the same laser pulse. In all other cases, interphoton times are distributed around a multiple of the repetition rate, that is, one peak every ~122 ns. For clarity, only the central three peaks are shown in Figure 3B. Previously, it was shown that the ratio of the number of photon pairs contributing to the central peak, N_c, to the average number of counts in the lateral peaks, $\overline{N}_\mathrm{l}$, can be used to measure the number of independently emitting chromophores.[6] Neglecting background, $N_\mathrm{c}/\overline{N}_\mathrm{l}$ ratios of 0.0, 0.5, 0.67, and 0.75 are expected for 1−4 molecules, respectively. From the distribution shown in Figure 3B, we determine an $N_\mathrm{c}/\overline{N}_\mathrm{l}$ ratio of $185/2981 = 0.062 \pm 0.006$. The nonzero background in SM measurements always produces a small contribution of detection events that fall in the central N_c peak. These can originate from background−background, signal−background, and background−signal detection pairs. Considering our experimental conditions (S/B $\approx$ 80) the determined $N_\mathrm{c}/\overline{N}_\mathrm{l}$ ratio of 0.062 corresponds to the expected ratio for a single emitter.[7] Figure 3A shows a sliding window analysis of the $N_\mathrm{c}/\overline{N}_\mathrm{l}$ ratio including 50000 photons for each data point while progressing in steps of 25000 photons (gray dots in Figure 3A). The low value of the ratio indicates that the system behaves as a single emitter throughout the transient. The increase of the $N_\mathrm{c}/\overline{N}_\mathrm{l}$ ratio as the fluorescence intensity drops during the course of the transient is expected as the S/B ratio decreases with the successive photobleaching of the chromophores.

From these experiments, it is clear that multiple chromophores of the dendrimer **1** can absorb light but that only one of the chromophores emits light at any given time. To explain why the system behaves as a single-quantum system, an efficient nonradiative pathway has to be present. A recent ensemble fluorescence upconversion study revealed a power-dependent 10-ps time constant, which was only present in multichromophoric dendrimers but not in the single-chromophore reference compound.[8] Accordingly, singlet−singlet annihilation was concluded to be the source of the power-dependent decay component. As this process is more than 2 orders of magnitude faster than the fluorescence decay (~4.3 ns), annihilation of multiple excitons is practically complete before fluorescence photons are emitted. Exciton annihilation is conceived as a Förster-type incoherent energy transfer from the excited donor to the excited acceptor molecule with the result of a doubly excited acceptor state. The latter can quickly relax to the singlet excited state. Observing a single multichromophoric system, efficient singlet−singlet annihilation is reflected by the fact that only one photon is emitted per laser pulse.

It is also interesting to note that the mean of the distribution of $N_\mathrm{c}/\overline{N}_\mathrm{l}$ ratios obtained from 44 molecules **1** of 0.07 ± 0.07 is substantially lower than the corresponding mean for single PI chromophores (0.14 ± 0.1). This can be explained by the higher S/B ratio obtained for **1** compared to that for the model compound.

For the first time, we demonstrated a direct method to distinguish between the number of absorbers and emitters in single multichromophoric molecules. This has been achieved by studying the same multichromophoric molecule under modulated excitation and subsequent circular polarized excitation conditions. The technique enables the direct observation of the efficiency of singlet−singlet annihilation processes in individual multichromophoric molecules, such as dendrimers and conjugated polymers. Finally, these observations demonstrate the potential of individual multichromophoric systems to serve as highly efficient single photon sources (the probability of generating one photon per laser pulse is ~10%), devices with many practical applications, for example, for quantum cryptography[9] and quantum computing.[6,10] An adequately designed multichromophoric system can have a very high absorption cross-section, while at the same time an efficient annihilation mechanism (99.3% in the dendrimer presented here) guarantees the emission of only one photon per laser pulse.

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